Comparison of Au and Ag nanoshells' metal-enhanced fluorescence

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A B S T R A C T

The average enhancement factors of Au and Ag nanoshells (NSs) were analyzed theoretically to compare their overall performances on metal-enhanced fluorescence. We used the Mie theory and dyadic Green's functions to calculate the excitation rate and apparent quantum yield of NS interacting with a plane wave and a dipole, respectively, and then to obtain the enhancement factor. Moreover, the average enhancement factor (AEF) of NS on the fluorescence of a nearby molecule was obtained by averaging all possible orientations and locations of the molecule with a constant distance from NS. Our results show that the maximum AEF of Au NS occurs at the wavelength of the dipole mode, which is broadband. In contrast, the maximum AEF of Ag NS is at the narrowband quadrupole mode. In addition, the Stokes shift effect on AEF was studied for Au and Ag NSs.

1. Introduction

Because of the surface plasmon resonance (SPR) behavior, a variety of applications of metallic nanoparticles utilizing the accompanying strong light scattering and absorption have been developed, particularly on the biomedicine [1,2]. For example, the scattering property of Au nanoparticles, so called the Faraday–Tyndall effect [3], can be applied for biomedical imaging [4]. In the past two decades, various metallic nanoparticles have been synthesized and studied. For example, Au and Ag nanoshells (NSs), a silica bead coated by a metallic shell, were developed [5–8]. Due to that their SPR bands are tunable by adjusting the shell thickness and core size; NSs attract a lot of attention, particularly for the applications in the near

infrared (NIR) regime. In nanophotonics, studying the Purcell effect that the spontaneous emission of an emitter (e.g. QD or molecule) can be influenced and modified by the environment including vicinal nanostructure has become an important issue. In particular, the Purcell factor of a plasmonic nanostructure is significantly large, relative to dielectric nanostructures, for the manipulation of a nearby emitter's emission [9,10]. Recently, using the SPR for the metal-enhanced fluorescence (MEF; or called surface enhanced fluorescence) becomes more interesting for enhancing the fluorescence of a fluorophore or quantum dot (QD) in the proximity of Au or Ag nanoparticles [9–17]. Moreover, the feasibility of MEF using NSs has been proven [5,8]. The other advantage of Ag or Au nanoparticle is to reduce the lifetime of molecular fluorescence dramatically, so as to increase the photostability and to reduce the photo-bleaching [11]. Indeed, SPR of Au or Ag nanoparticles can enhance the local electric field as they are illuminated by an incident light. Although Au and Ag nanostructures possess the SPR induced near-field enhancement, a

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quenching for molecular fluorescence could happen due to the energy transfer between the molecule and metallic nanoparticle. Therefore, a proper distance between them needs to be kept to avoid the quenching [18–20]. In fact, a few reports have shown the quenching effect of Au nanoparticles on molecular fluorescence, rather than the enhancement [21,22]. However in some previous numerical analyses, the maximum enhancement factor (EF) was always calculated by considering the optimal location and orientation of molecule only. As a result, the overall performance of Au NS could be overestimated [23–27].

The purpose of this paper is to study the average enhancement factor (AEF) of the Au and Ag NSs theoretically on MEF by taking into account the arbitrary orientation and location of a molecule in the proximity of NS [28–30]. In particular, the Stokes shift effect of molecular fluorescence on MEF of NS is investigated. To the knowledge of authors, the AEF is useful to evaluate the overall Purcell effect of a large number of NSs on molecular fluorescence without overestimating their performances.

2. Theory

Fig. 1 shows the configuration of Au or Ag NS, a silica bead coated by a metal layer, illuminated by an x-polarized plane wave of UV to NIR regime, where a molecule (an electric dipole) near the NS with a distance d. Without loss of generality, we assume the incident wave propagates along the z-axis with x-polarization. The radius of silica core and the outer radius of shell are denoted by a_2 and a_1, respectively. The thicknesses of the metal shell is denoted by t, where $t = a_1 - a_2$. The material indexes of the surrounding medium, metallic shell, and silica core are denoted by 1, 2, and 3 respectively. The origin of the coordinates is located at the center of the silica bead. To analyze the performance of NS on MEF, the process of
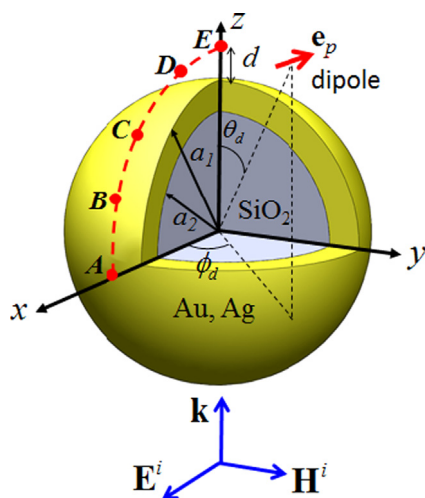

Fig. 1. Configuration of a molecule (dipole) near a NS illuminated by a polarized plane wave. The radii of silica core and the outer shell are denoted by a_2 and a_1, respectively. Five typical points (A, B, C, D and E) are in the x–z plane with the same distance d from NS, where the molecule could be located.

molecular fluorescence is simply divided into two stages: the excitation and the emission stages [9,28–30]. In the excitation stage, the enhanced electric field around NS provides a strong excitation rate for a nearby molecule. Once the molecule is excited, it starts to emit the fluorescence at the emission stage, and the emission is also affected by the nearby NS. At this stage, the molecule can be modeled as an electric dipole. In the following, the roles played by NS at each stage will be discussed individually, and then the overall EF for the whole process will be studied. To analyze the MEF of NS, the process of molecular fluorescence is simply divided into two stages: the excitation and the emission stages. In the excitation stage, the enhanced electric field around NS provides a strong excitation rate for a nearby molecule. Once the molecule is excited, it starts to emit the fluorescence under the influence of the nearby NS at the emission stage. At this stage, the molecule can be modeled as an electric dipole. The roles played by NS at each stage are discussed individually, and then the overall enhancement factor (EF) for the whole process is studied.

2.1. Excitation rate of NS on a molecule

Mie's theory [28–33] of a layered sphere is used to calculate the electric field induced by the interaction of an incident plane wave with NS. Because the local electric field is enhanced around NS due to SPR, the intensified electric field can increase the probability for exciting the molecules in the proximity of NS. The excitation rate of NS on a molecule at a specific excitation wavelength λ_{ex} is defined as

$$\Psi(\mathbf{x}_d, \mathbf{e}_p; \lambda_{ex}) = |\mathbf{E}(\mathbf{x}_d; \lambda_{ex}) \cdot \mathbf{e}_p|^2 / |\mathbf{E}^i|^2 \qquad (1)$$

where $\mathbf{x}_d$ is the position vector of the molecule, and $\mathbf{e}_p$ is the unit vector of the molecular dipole moment. Here, the $\mathbf{E}$ is the total electric field in the medium, which is the linear combination of the incident and scattered fields, $\mathbf{E} = \mathbf{E}^i + \mathbf{E}^s$. The denominator in Eq. (1) is the intensity of the incident wave.

2.2. Apparent quantum yield of an emitting molecule affected by NS

After the molecule is excited, it is modeled as an oscillating electric dipole in the following emission stage. Since the dipole is in the proximity of NS, its radiative and nonradiative powers should be affected by the NS. The unit vector of the dipole moment, $\mathbf{e}_p$, can be decomposed into two components: one is along the radial direction, and the other is along the tangential direction in the spherical coordinates. Two sets of dyadic Green's functions are derived analytically by using the series solutions in terms of spherical wave functions [34,35] to calculate the electromagnetic fields induced by an arbitrarily oriented dipole interacting with NS: one is for a unit radial dipole, and the other is for a unit tangential dipole. The total electromagnetic fields generated by this arbitrarily oriented dipole in the presence of the NS are the linear combinations of the electromagnetic fields of the two sets of Green's functions. As a result, the radiative decay rate P_r